Pest Management Grants Final Report

98-0258

Use of Lime Sulfur for the Control of Postharvest Mold of Citrus Fruit

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DISCLAIMER

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Table of Contents

Use of lime-sulfur solution for the control of postharvest mold of citrus fruit

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SUMMARY

Postharvest green mold of lemons was reduced by more than 98% by immersion of fruit in 3% lime sulfur solution for four minutes at commercial citrus packinghouse (Mayflower, TCLA in Porterville). Fruit was rinsed after treatment compared to non-rinsed fruit and loss of effectiveness was evident. Lime sulfur treatments were compared with 3% sodium bicarbonate and 200 ppm chlorine and chlorine alone in water, and both treatments were far superior than chlorine alone. Post treatment rinsing the fruit in earlier tests appeared to lower effectiveness of carbonate salts, however, rinsing did not appear to reduce the effectiveness of lime sulfur. Because of concerns for odor portable fans were placed in areas to exhaust odors outside. If a permanent use for lime sulfur solution is sought, an exhaust covering on the top of the tank would be desired. Packinghouses should have stainless steel tanks and conveyors to avoid corrosion problems as well as a stainless heat exchanger inside the tank.

The solution when discarded from the tank can be land disposed as a soil conditioner.

Green mold of citrus, caused by *Penicillium digitatum* is one of the most economically important postharvest diseases of citrus worldwide. In California, losses of about 2% and 5% of orange and lemons, respectively, occur each year in storage. The primary infection courts of *P. digitatum* are wounds on fruit inflicted during harvest and subsequent handling. Eradication of these infections is required to achieve acceptable levels of control. Currently, green mold is controlled in the United States by applications of the fungicides ortho-phenyl phenate, imazalil, and thiabendazole. New methods are needed because pathogen resistance to these chemicals has developed, and regulatory issues and public concerns about health risks of ingesting fungicide residues threaten the continued use of fungicides in the future. We evaluated compounds that have well studied environmental and animal toxicological properties and extensive precedents as additives or natural components in foods. By selecting these compounds, we hope to facilitate their approval by minimizing health, environmental and disposal issues. A cleaning process that meets these criteria is the immersion of fruit in heated solutions of sodium carbonate or bicarbonate, a practice first described about seventy years ago. Although we found it worked well, disposal of the high pH and sodium content solutions after use can prohibit their use in some locations. Therefore, we evaluated many other compounds, and found that lime-sulfur solution, first described in the early nineteenth century and one of the oldest fungicides, worked well in repeated tests. A yellow-orange solution, 10.6lbs/gallon and pH 11.5, it is a mixture of CaS•Sx (calcium polysulfide and small amount of calcium thiosulfate). It is prepared by combining hydrated lime (Ca•H2O) with elemental sulfur. It releases small amount of hydrogen sulfide and when diluted below 1.5% (wt/vol) or at lower pH, it oxidizes to sulfate and calcium with elemental sulfur precipitation or "blooms". It is stable for many months in 29% a.i. calcium polysulfide in "Liquid Lime Sulfur Solution" formulations. Lime sulfur solution is used to open sewer lines, immobilize metal ions and salts in mine soil remediation, adjust soil pH down, and improve water penetration properties of soil. As a pesticide, first described in 1802 by Forsyth, King's gardener in England, for control of mildew. The present lime sulfur formula was standardized in 1850, by Grison, head gardener at Versailles and is the same formula used to this day. "Grison's Liquid" was in common use by 1900 for apple scab, powdery mildew, San Jose scale, aphids, mites, brown rot of peaches, and other pests and diseases. It is used below 26°C in field applications to minimize phytotoxicity to foliage. Most safety concerns are from hydrogen sulfide evolution. OSHA limits for hydrogen sulfide are 10 ppm workplace (8 hours) and 15ppm short term (15 minutes). Lime-sulfur solution has acute but no chronic toxicity hazard or carcinogenicity, and its oral LD50 (rat) is 820 mg/kg. It is moderately irritating to skin.

MATERIALS AND METHODS

Standard methods used to evaluate citrus postharvest fungicides were used (Eckert, J. W., and Brown, G.E. 1986 Evaluation of postharvest treatments for citrus fruits. Pages 92-97 in: Methods for Evaluating Pesticides for Control of Plant Pathogens. K.D. Hickey, ed. American Phytopathological Society, St. Paul, MN.) Lemons and oranges used in all experiments were California grown and selected by hand from field bins after harvest, before any commercial postharvest treatments were applied. Lemons selected were light green to pale yellow in color and used within one or two days. Petri dishes of potato dextrose agar were inoculated with *P. digitatum* isolate M6R (from J.W. Eckert, University of California, Riverside) and incubated at 20°C for 1 to 2 weeks. Spores were rubbed from the agar surface with a glass rod after a small volume of sterile 0.05%Triton X-100 was added. The spore suspension was passed through two layers of cheesecloth and diluted with sterile water to density of 0.1 at 420 nm. This density contains approximately 1 million spores per ml and is recommended for evaluation of postharvest treatments to control green mold. Each fruit was wounded and inoculated once by dipping a stainless-steel rod in the spore solution and making a puncture injury 1mm wide by 2 cm deep on each fruit. The shallow wounds penetrated the albedo tissue but not the juice sacs and simulated natural inoculation. After inoculation, the fruit were incubated at 24 hours at 16 to 20°C, then the treatments were applied. The lemons were treated in plastic baskets in four or five replicates of 25 fruit each, rinsed with water, placed in plastic cavity trays, and stored 1 or 2 weeks at 15 to 20°C before the incidence of green mold infected fruit was counted.

In this report, our objective is to present the results that indicate lime-sulfur solution works effectively for citrus fruit postharvest applications, and to evaluate variables associated with its practical use, such as the influence of no rinse versus rinse using a lime sulfur solution and injury to fruit.

In the commercial test the fruit was introduced into the soak tank and allowed to progress through the tank and up the conveyor into the brush bed. The treatments of fruit were picked up prior to the waxer (which has a fungicide in the wax). For the non-rinsed treatment the hot water was turned off and the fruit removed. On the rinsed treatment the fruit was allowed to progress through the rinse water, (approximately 1 gal per minute per nozzle which is a fairly standard rinse application) and then picked up prior to the waxer.

The chlorine alone treatment was dipped in the flow through dump tank, with a chorine concentration of 200 ppm, these treatments were dipped by means of an 8lb. mesh bag. The 3% sodium bicarbonate and 200 ppm chlorine solution was dipped in the flooder tank at Mayflower TCLA, for 4 ½ minutes by means of an 8lb mesh bag. All treatments were dipped for a period of 4 ½ minutes to reflect the time the lime sulfur treatments were in the soak tank. During tests on the commercial line at Mayflower TCLA fruit was processed at the rate of 75 bins per hour. During the entire week of fruit processing at 600 bins per day and 5 days a week, approximately 3,000 bins were processed through the tank. With a gross value of $1,440,000 after storage and a utilization value of $936,000. In this commercial test an emphasis was made to determine how the odors of the lime sulfur affected packinghouse personnel. The hydrogen sulfide was not detectable on either a Drager or Sensidyne dosimeter, however, interviews were conducted with 6 packinghouse personnel who noticed odors upon charging the soak tank with liquid lime sulfur. After a few minutes use the odor wasn'7t considered as objectionable and after a week's use, not objectionable at all. Many tests for odor have been done (two at Lindcove previously and one at TCLA) the past three years and none have exceeded the OSHA levels. All measurements have been below detection in the packinghouse. (Attached will be drawings of a tank hood complete with exhaust system). This was to finally alleviate any safety concerns. In the test at Mayflower TCLA to examine several variables on lime sulfur solution effectiveness and to compare it to other treatments, lime sulfur solution was at 3% with a tank residence time of 4 ½ minutes. The treatments included 1) treated but inoculated; 2) immersion in lime sulfur solution for 4 ½ minutes but not rinsed; 3) immersion in lime sulfur solution for 4 ½ minutes and rinsed with approximately 1 gallon per minute per nozzle, with 10 nozzles on the rinse bar; 4) immersion in a solution of sodium bicarbonate with 200 ppm sodium hypochlorite; 5) immersion in a water tank for 4 ½ minutes with 200 ppm sodium hypochlorite. The test was done with lemons, randomized and stored at 10 degrees C (52 degrees F) for two weeks at the Lindsay Sunkist coolers. Then the incidence of green mold was then determined.

The lime sulfur solution was provided by Best Sulfur Products, 5427 E. Central Ave., Fresno, California 93725. It contained by weight 29% calcium polysulfide. The treatment solutions were prepared by dispensing lime sulfur solution usually at 3% by weight to volume in the stainless tank at Mayflower TCLA. The active concentration of calcium polysulfide in a 3% W/V lime sulfur solution is 0.87%. The effectiveness of lime sulfur solution was compared to a sodium bicarbonate solution with 200ppm sodium hypochlorite and to sodium hypochlorite solutions whose efficacy for green mold has been well investigated.

RESULTS

The incidence of green mold was reduced by immersion in a 3% wt/vol. lime sulfur solution at 105°F for 4 ½ minutes. No injury was observed after storage on lemons. The effectiveness of a 3% lime sulfur solution was not significantly different than the 3% sodium bicarbonate 200ppm chlorine solution. However, both treatments were superior to chlorine and water alone for 4 ½ minutes, and water alone for 4 ½ minutes. Lime sulfur reduced green mold by 100% when not followed by a water rinse, and 98.98% for the rinsed fruit. Sodium bicarbonate and 200ppm chlorine reduced green mold by 98.87%. (Table 1) Sodium hypochlorite alone at 200ppm reduced green mold by 31.7%. Water alone reduced green mold by 1.7%. All treatments used immersion for 4 ½ minutes in each solution.

DISCUSSION

There have been several prior tests that have demonstrated lime sulfur without a postharvest rinse was an effective treatment. No fruit injury has occurred from not washing the lime sulfur solution off. In terms of resistance management and fungicide use it could be an effective tool to implement for packinghouse processing. Tests done in 7/17/97 at the USDA-ARS Fresno with no rinse using a 3% lime sulfur solution yielded a 96% decay control on green mold. Tests with no rinse done on 9/8/98 yield 96% decay control on green mold. In September 30, 1998 at Lindcove field station the 3% lime sulfur solution yielded 99.3% decay control on lemons at 110°F.

Lime sulfur solutions are extremely effective decay control tools for citrus, however long term implementation requires government help as well as packinghouse buy in. Reasons for government help would include aid to houses for equipment upgrades, implementing the use of the potassium polysulfide use over calcium polysulfide. Potassium polysulfide as demonstrated in Table 2 works effectively as calcium polysulfide, however it does not form the scale on equipment or heat exchanger as does the calcium product. Government help would help industry to look at this alternative of the potassium polysulfide.

Secondly, there is dual disposal for the use of lime sulfur solutions, in the tank it is considered a pesticide, however when disposed of on land it is a soil supplement. This type of chemical use should be highly encouraged by government and industry in the form of incentives for its use.

The most awkward part of calcium polysulfide is the odor. Exhausts and/or fans to remove odors would be helpful. Isolation to an area of the packinghouse where personnel are limited would be helpful. Covering soak tanks with tarps would be helpful as long as exhausts were operating.

The calcium polysulfide breaks down on the peel of the fruit to calcium and sulfur. There is relatively low toxicity to humans, in fact some old time remedies for its use were, acne on humans and mange on animals.

The history of the lime sulfur solution goes back almost 200 years. It is listed in the Merck Index under Vleminckx's solution. Not much is understood as to the exact method of fungicidal action. One possibility is $CaSx + H2O + CO2 \rightarrow H2S + CaCO3 + 4S$ which may be further oxidized to: $2S+3O2 \rightarrow H2O \equiv H2SO4$ with sulfuric acid being the final product. The three prevailing theories of fungicidal action are:

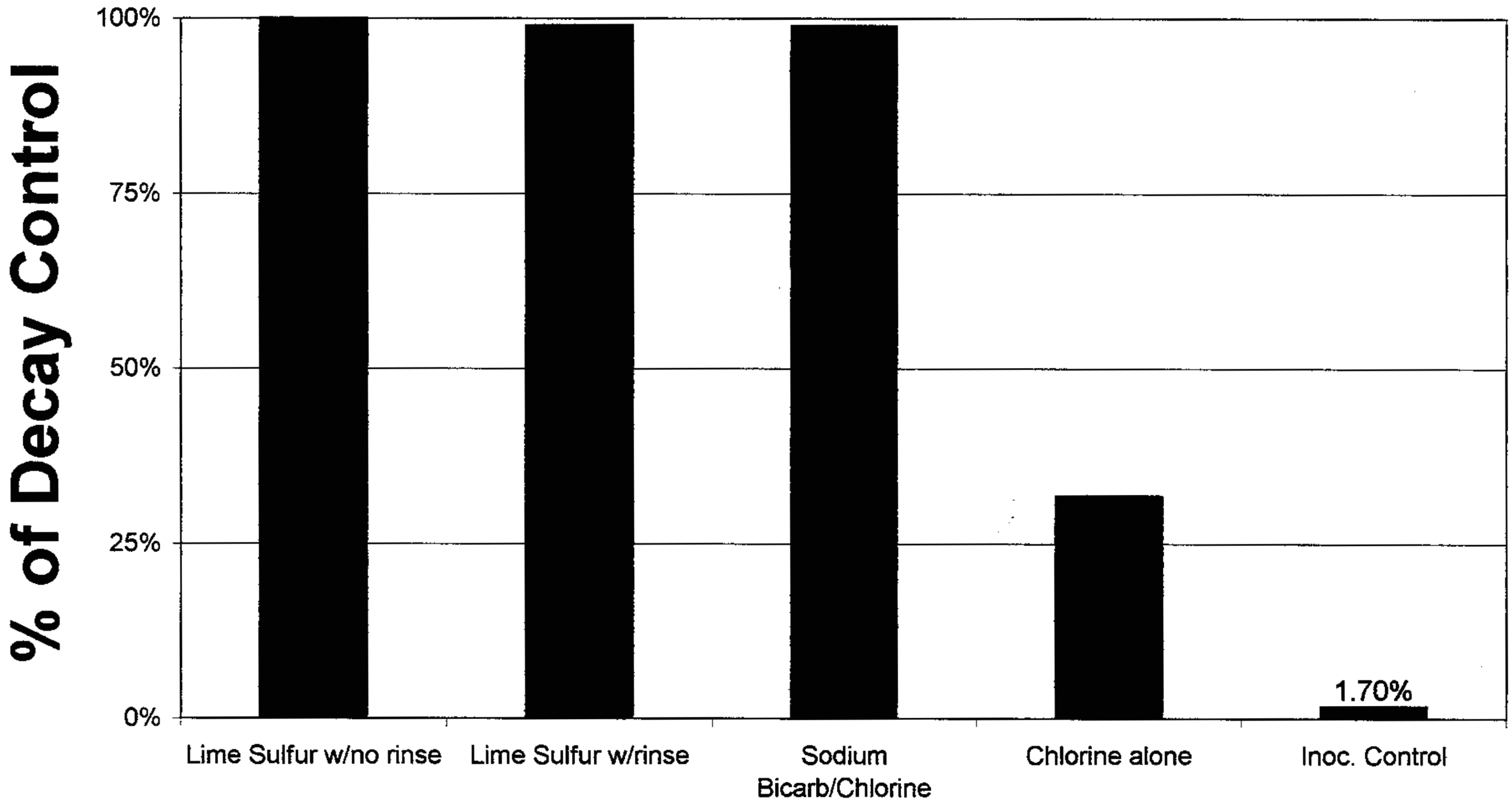
1) Direct action by sulfur itself
2) Oxidation theory: elemental sulfur is oxidized to sulfur dioxide, sulfur trioxide, pentathionic acid or other possible oxidation products
3) Hydrogen sulfide, elemental sulfur is reduced to hydrogen sulfide which is the toxicant.

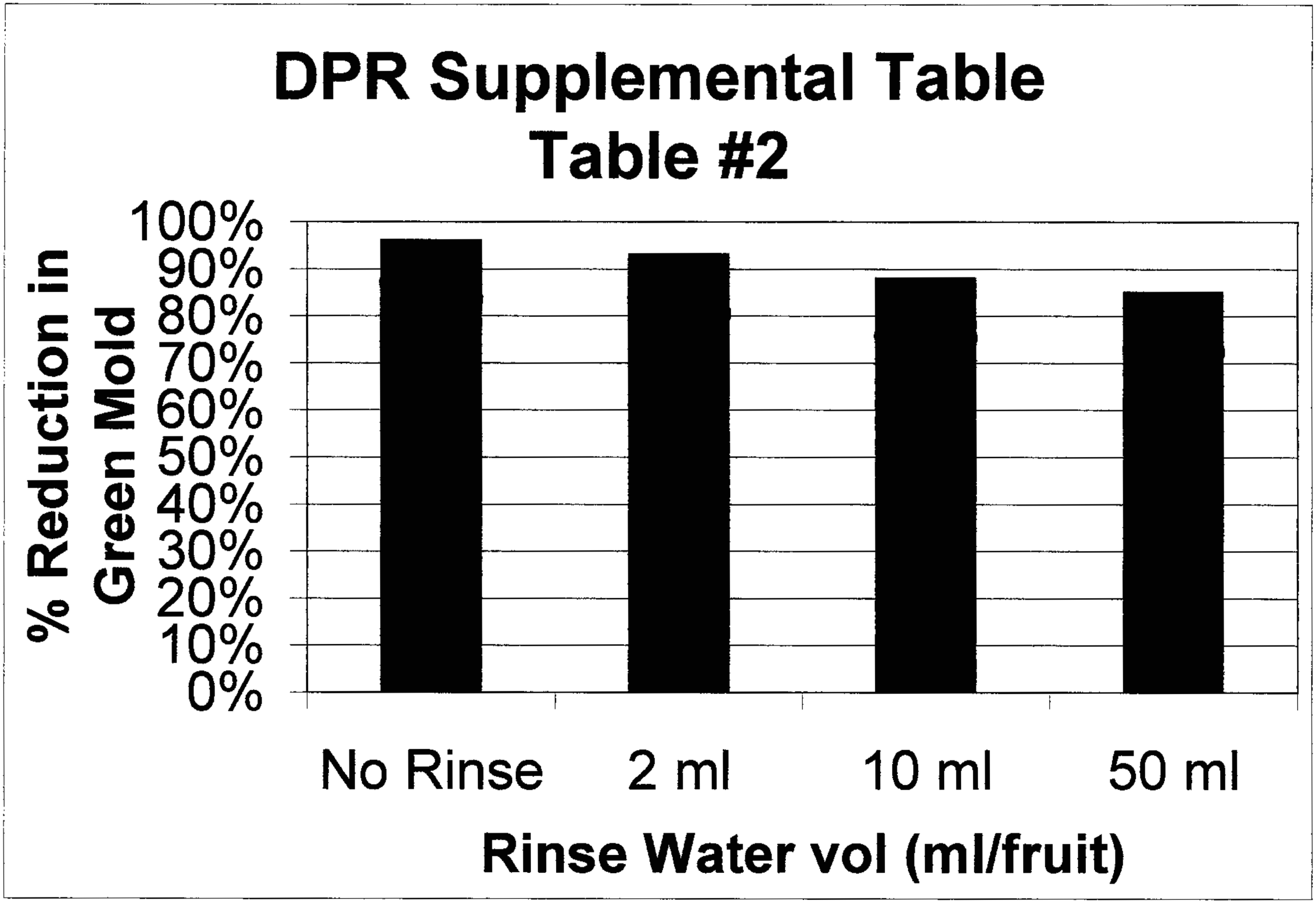
Sulfur with its multifaceted threat for fungicidal action against spores, bacterium and other types of pathogens it remains an ideal solution for citrus packinghouse soak tank solutions.

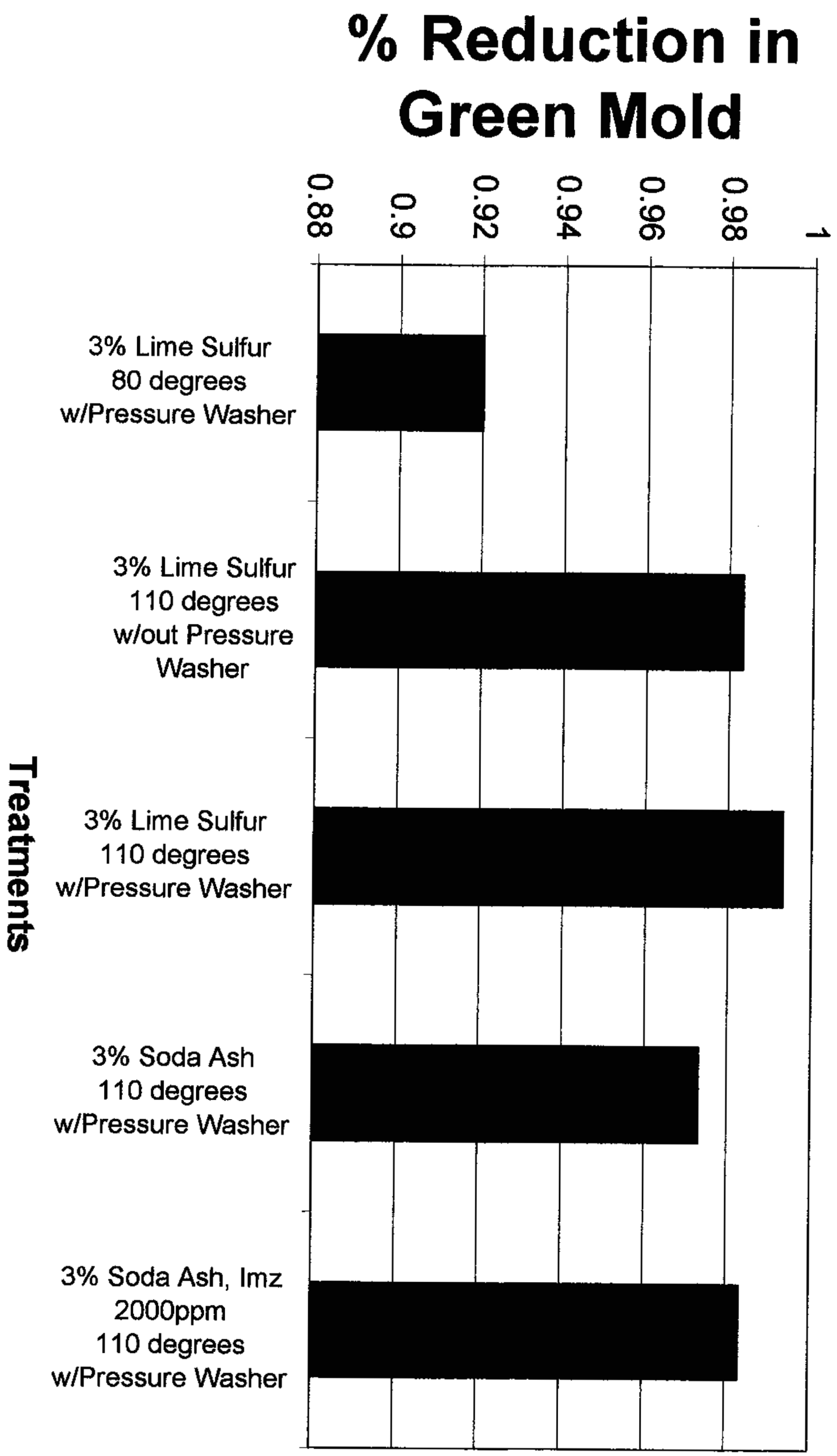
Explanation of Graphs:

1. Table1 is the results of the DPR grant test at Mayflower-TCLA. Results indicate a no rinse treatment is best for decay control. This is followed by lime sulfur with a normal rinse, and sodium bicarbonate, 200ppm chlorine treatment followed by chlorine alone.
2. Table 2 demonstrates the effectiveness of a no rinse using lime sulfur. A "normal rinse" is where 10ml of the water per second is used. You can clearly see that with increasing the rinse the decay control efficacy goes down.
3. Table 3 indicates that a 110° F lime sulfur alone is as good as soda ash followed by Imazalil, also that the efficacy improves with temperature. In this test the pressure washing the fruit after treatment did not reduce its efficacy.
4. Table 4 compares lime sulfur solution to many standard treatments such as soda ash (sodium carbonate), Knapp's Fruit Wash (neutral cleaner), ammonium phosphates, sodium phosphates, and potassium carbonates. Lime sulfur in this test indicates it is equal or superior to many treatments.
5. Table 5 is another study using lime sulfur and its sister compound potassium polysulfide and comparing it to known treatments. In this test Borax/Boric acid, soda ash, thiourea, calcium thiosulfate were compared to the two polysulfide compounds. Both compounds compared favorably to the industry standard treatments of Borax/Boric acid and soda ash.
6. Table 6 shows a study using some known food preservatives, organic salts, and comparing them to lime sulfur, and soda ash. Potassium sorbate, sodium benzoate, and potassium benzoate compared favorably to lime sulfur and even slightly superior in this test to lime sulfur.

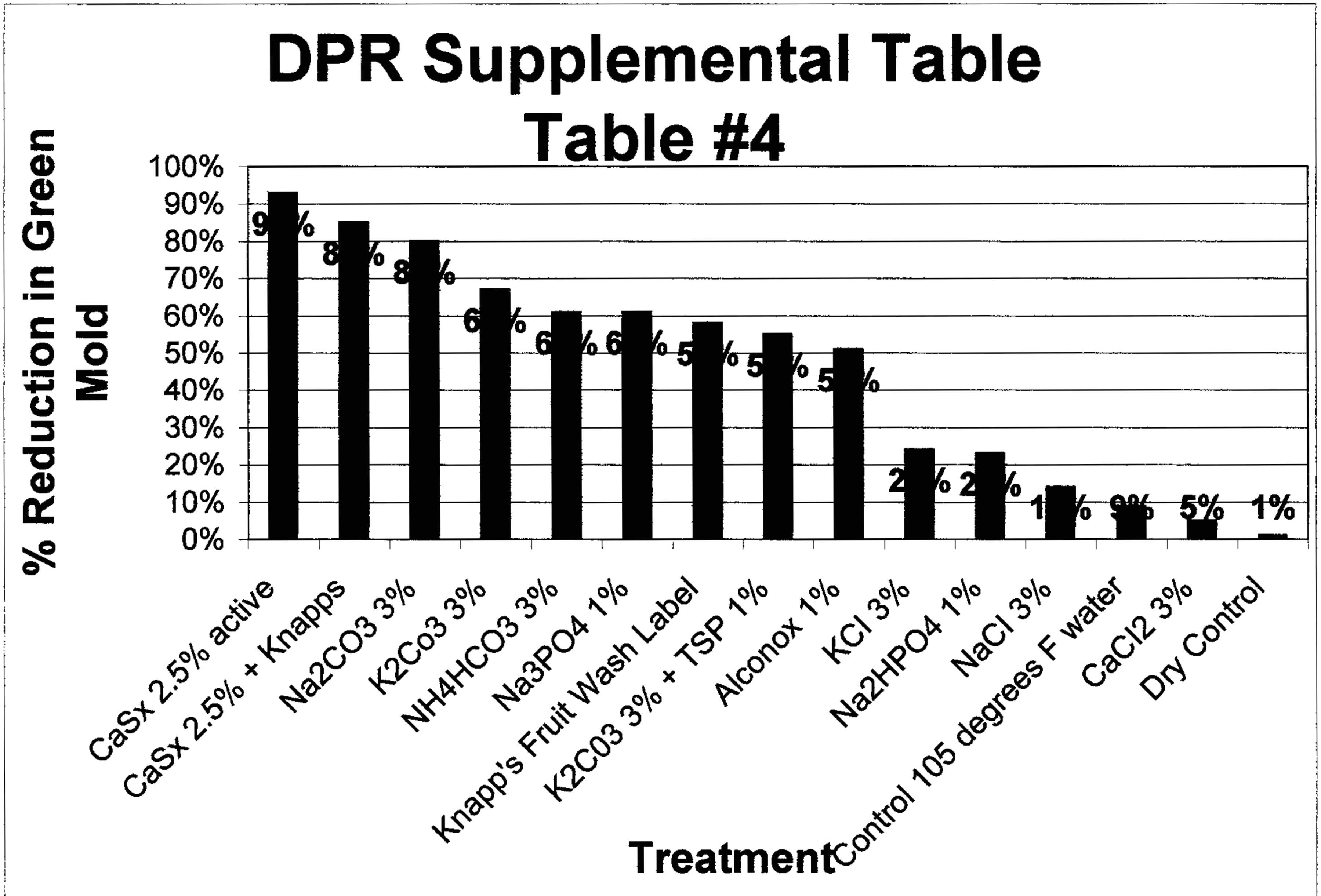
DPR Grant Test - March 2000
Table #1

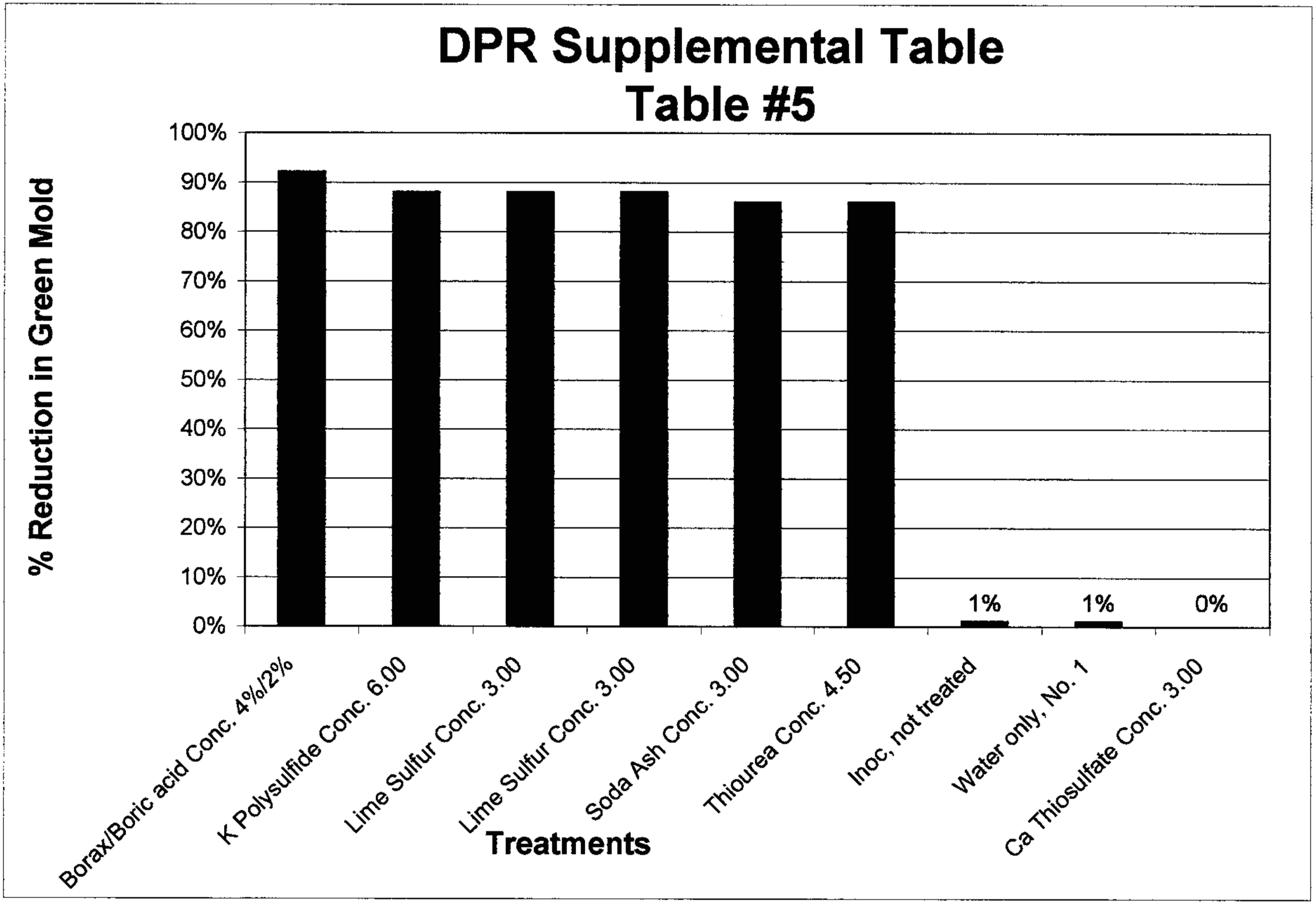


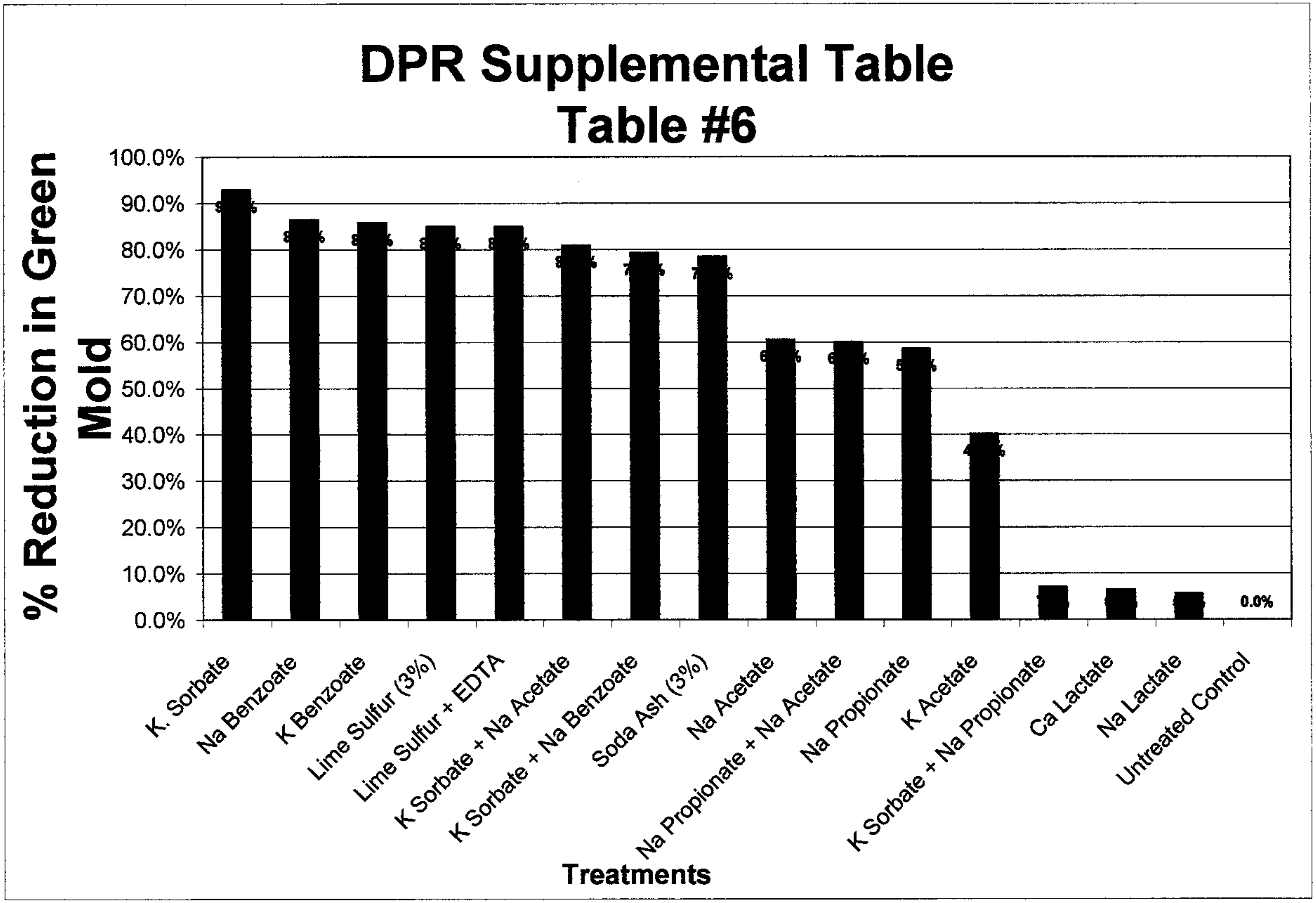

DPR Supplemental Table
Table #2
% Reduction in Green Mold
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
No Rinse
2 ml
10 ml
50 ml
Rinse Water vol (ml/fruit)



DPR Supplemental Table
Table #3


DPR Supplemental Table
Table #4
% Reduction in Green Mold
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
9%
5%
1%
CaSx 2.5% active
CaSx 2.5% + Knapps
Na2CO3 3%
K2Co3 3%
NH4HCO3 3%
Na3PO4 1%
Knapp's Fruit Wash Label
K2C03 3% + TSP 1%
Alconox 1%
KCl 3%
Na2HPO4 1%
NaCl 3%
Control 105 degrees F water
CaCl2 3%
Dry Control
Treatment


DPR Supplemental Table
Table #5
% Reduction in Green Mold
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1%
1%
0%
Borax/Boric acid Conc. 4%/2%
K Polysulfide Conc. 6.00
Lime Sulfur Conc. 3.00
Lime Sulfur Conc. 3.00
Soda Ash Conc. 3.00
Thiourea Conc. 4.50
Inoc, not treated
Water only, No. 1
Ca Thiosulfate Conc. 3.00
Treatments


DPR Supplemental Table
Table #6
% Reduction in Green Mold
100.0%
90.0%
80.0%
70.0%
60.0%
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
0.0%
K. Sorbate
Na Benzoate
K Benzoate
Lime Sulfur (3%)
Lime Sulfur + EDTA
K Sorbate + Na Acetate
K Sorbate + Na Benzoate
Soda Ash (3%)
Na Acetate
Na Propionate + Na Acetate
Na Propionate
K Acetate
K Sorbate + Na Propionate
Ca Lactate
Na Lactate
Untreated Control
Treatments

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